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ALUMINUM OXIDE CERAMIC FIBERS AND MATERIALS BASED ON THEM

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The continual growth of the working temperatures of modern aircraft and gas-turbine facilities requires increasing the performance characteristics of ceramic, including heat-shielding and heat-insulating, materials. Materials based on aluminum oxide fibers show the greatest promise for use at temperatures to 1750°C. Different types of fibers developed at the FGUP VIAM and their particularities and use in materials are examined. Different types of fibrous heat-shielding and heat-insulating materials and their technical and operating characteristics are also presented.

Key words: ceramic materials, fibers, aluminum oxide, heat-shielding materials, working temperature, strength, density, thermal conductivity.

Of recent interest in the use of high-temperature construction materials is that attention has shifted from metal to nonmetal materials. The best known heat-resistant alloys cannot operate for a prolonged period of time at temperatures above 1100 – 1200°C. The high specific mass of metal alloys, degradation of the mechanical properties at elevated temperatures (600 – 900°C), limited service life and high prices for components such as Co, Ni, Cr, W, Ti, Mo, Re and others greatly lower the efficacy and profitability of their use. For prolonged exposure (hundreds to several thousands of hours) to high temperatures above 1200°C in an oxidative medium, ceramics are the only available materials and they have good durability and excellent anticorrosion properties [1].

For new-generation prospective engineering articles it is necessary to develop materials with a wide range of properties meeting user requirements. To develop new-generation articles for hypersonic aviation, aerospace and rocket technology it is necessary to develop heat-shielding materials that can function at high temperatures and that have high mechanical strength, low dielectric constant and low dielectric losses, and high erosion resistance in flights at hypersonic speeds.

Today, ceramic composite materials and high-temperature heat-shielding based on oxide fibers, first and foremost, aluminum oxide fibers, are being actively developed worldwide. Such fibers are given priority because of their exceptional oxidative stability above 1200°C, chemical inertness with respect to most matrix materials, low specific mass and high elastic modulus (in the case of α-Al_2O_3).

Many companies in the leading countries of the world, first and foremost, those specializing in building automobiles and aviation technology, are working to develop fibrous ceramic materials based on aluminum oxide fibers — ICI PLC (Imperial Chemical Industries, Great Britain) [2], 3M (Minnesota Mining and Manufacturing Company, USA) [3], Boeing Company (USA) [4], Zircar Ceramics Inc. [5], The Carborundum Company (Unifrax, USA) [6], Aerospatiale Societe Nationale Industrielle (France) [7], Mitsubishi Corporation (Japan) [8], and others.

Fiber heat-shielding based on oxide fibers has taken a firm position in the market for heat-shielding materials. The principal advantages of this class of materials are low density, which permits a considerable reduction of the mass of thermal facilities, and a high degree of heat-insulation and resistance to oxidation at high temperatures. The possibility of obtaining discrete and continuous aluminum oxide fibers from 1 to 20 μm in diameter by the sol-gel technology allows the manufacture of a wide assortment of heat-shielding materials with different density, both flexible and rigid, thread, fabric, cord and other packing materials.

Light-weight rigid heat-insulating and heat-shielding fibrous materials comprise a spatial framework consisting of highly heat-resistant fibers, where the pores in the material occupy more than 90% of the volume. As a result, they are used primarily in applications where the critical parameter is the mass of the thermal insulation, i.e., in aviation, space and rocket engineering. However, their drawback is low strength due to the brittle nature of ceramic. Hardening such materials

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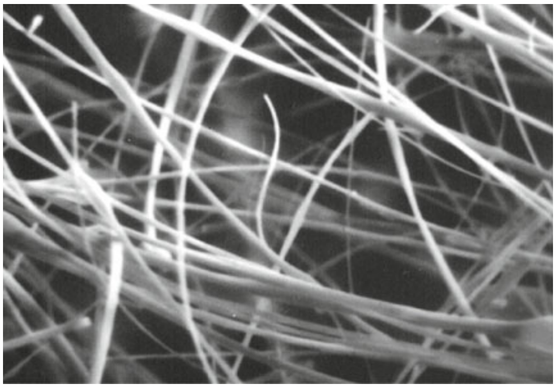

Fig. 1. Photomicrograph of discrete fibers with the composition Al_2O_3–SiO_2, SEM; ×1000.

Fig. 2. Discrete Al_2O_3-based amorphous fiber (overall view).

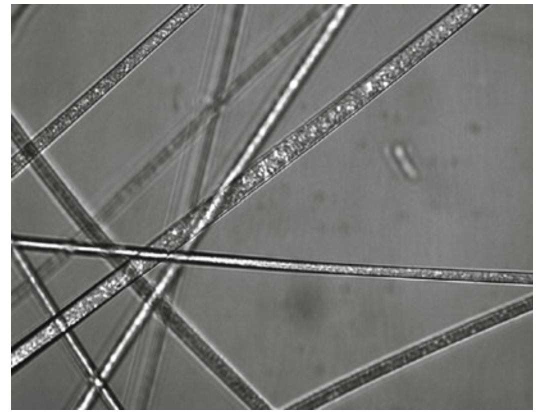

Fig. 3. Photograph of continuous Al_2O_3 fibers; optical microscope, ×300.

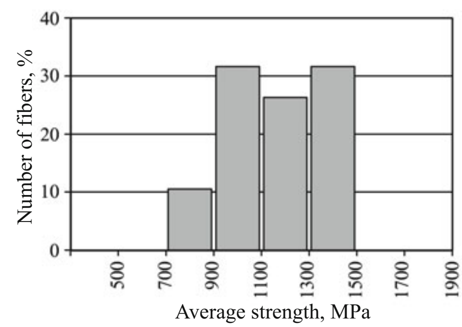

Fig. 4. Histogram of the strength distribution of continuous Al_2O_3 fibers.

is one of the many problems that developers are working to solve.

Dense ceramic reinforced with aluminum oxide fibers is capable of demonstrating excellent strength and durability at temperatures to 1200°C, 20% lower density, and an order of magnitude lower thermal conductivity as compared with monolithic ceramic [9]. For these reasons, composites of this type are also given priority in aviation and space engineering for manufacturing parts used in turbo aircraft engines [10 – 12].

Complex studies in the development of a technology for manufacturing discrete fibers for creating heat-insulating materials have led to the development of Al_2O_3–SiO_2 fibers, which give long-term service at temperature 1650°C and short-term service at 1750°C. The external appearance of discrete fibers, as observed in a scanning electron microscope (SEM), is displayed in Fig. 1. The average diameter of the discrete fibers is 3 μm, and the phase composition after standard heat-treatment is mullite + δ-Al_2O_3.

Amorphous fibers made from aluminum oxide with elastic modulus less than 150 GPa were developed in order to obtain samples of a complex continuous thread and flexible packing materials from discrete fibers (Fig. 2).

Continuous aluminum oxide fibers with different compositions have also been developed at VIAM. Continuous fibers are intended for use as reinforcing fillers and thread for sewing heat-insulating materials, for high-temperature textile articles (packing cord, heat-shielding fabrics), used in the manufacture of structural elements for rockets, aviation and space technology, and functions at temperatures to 1700°C. The chemical and phase composition of such fibers is determined by their function. Continuous fibers have a larger diameter, equal to 8 – 16 μm, than discrete fibers.

The composition for reinforcing continuous aluminum oxide fibers was chosen with at least 99% Al_2O_3, which gives the greatest tensile strength. The maximum fiber strength attained was 3020 MPa; the average strength was 2200 MPa. The phase composition of the fibers is δ-Al_2O_3.

Fibers whose principal phase is α-Al_2O_3 were obtained in order to increase the chemical resistance and elastic modulus of the fibers. The average strength of these fibers is 1200 MPa and the maximum strength is 1500 MPa; the elastic modulus is greater than 300 GPa. The external appearance of the continuous fibers and their strength distribution are presented in Figs. 3 and 4. A drawback of fibers of this kind is low working temperature, equal to 1000°C.

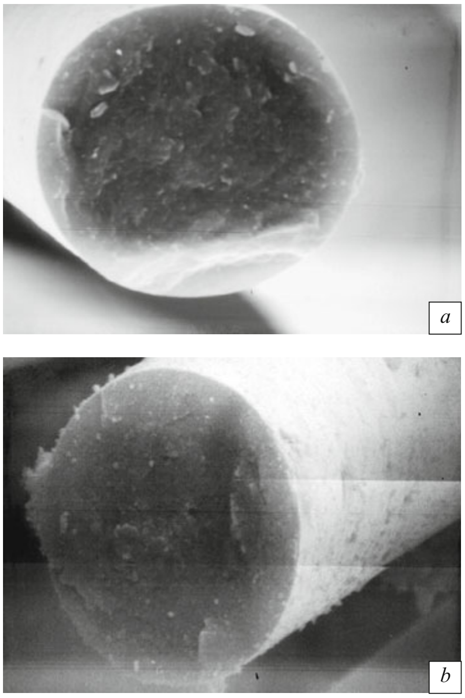

Fig. 5. SEM photograph of continuous fibers (×8000): *a*) mullite, δ-Al_2O_3, α-Al_2O_3; *b*) δ-Al_2O_3, α-Al_2O_3.

Fig. 6. Flexible heat-insulating material (overall view).

Continuous polycrystalline fibers based on the system Al_2O_3–SiO_2 have been developed for high-temperature heat-shielding materials with working temperature to 1700°C. The average strength of fibers with this composition is 1500 MPa. The elastic modulus of such fibers is less than for Al_2O_3 fibers and constitutes 187 – 210 GPa, while the working temperature is considerably higher and reaches 1700°C. This combination of properties makes it possible to successfully use these fibers for flexible heat-insulating materials. The phase composition of the fibers is a mixture of mullite and high-temperature phases of aluminum oxide.

TABLE 1. Basic Properties of Aluminum Oxide Fiber Based Flexible Materials

Material	Density, g/cm^3	Linear shrinkage (1600°C, 24 h), %	Thermal conductivity (1300°C, 105 Pa), W/(m · K)	Working temperature, °C
VTI-19	0.08 – 0.12	≤5.0	0.32	1700
VTI-20	0.18 – 0.23	≤5.0	0.34	1700
VTI-21	0.27 – 0.33	≤5.0	0.32	1700

TABLE 2. Properties of VMK-5 and VMK-6 Materials

Property	VMK-5	VMK-6
Density, kg/m^3	500 ± 50	1000 ± 50
Ultimate compression strength, MPa, not less than	1.0	2.0
Working temperature, °C	1550	1550

Continuous polycrystalline fibers based on the system Al_2O_3–SiO_2 and Al_2O_3 are displayed in Fig. 5.

Fibers containing low-temperature metastable phases of aluminum oxide and amorphous SiO_2 are used to make textile articles from fibers based on the system Al_2O_3–SiO_2. Such fibers possess a smaller elastic modulus than high-temperature polycrystalline fibers and undergo textile processing more easily. The average value of the elastic modulus is 90 GPa, and the tensile strength is 1300 MPa. These fibers have been used as a basis for developing a technology for manufacturing primary and simply twisted threads with linear density from 10 to 300 tex.

In recent years, high-temperature heat-shielding and heat-insulating materials in a wide range of densities (rigid and flexible) based on aluminum oxide fibers with working temperature to 1700°C have been developed at VIAM.

Properties of TZMK-1700 Rigid Heat-Insulating Materials

Working temperature, °C . . . . 0.25 – 0.3
Density, g/cm^3 . . . . –110 ± 1700
Thermal conductivity (at 20°C), W/(m · K). . . . . . ≤0.09
CLTE, 10^{-6} K^{-1} . . . . 6 – 7
Compression strength in “weak” direction (10% deformation), MPa . . . . ≥0.2
Lineal shrinkage (at 1600°C, 24 h), % . . . . ≤3

The exterior appearance of flexible heat-insulating material based on aluminum oxide is shown in Fig. 6, and the properties of such materials are presented in Table 1.

Discrete aluminum oxide fibers have been used to develop the ceramic composite materials VMK-5 and -6 with working temperature to 1550°C (Table 2). The structure of the VMK-5 material is shown in Fig. 7.

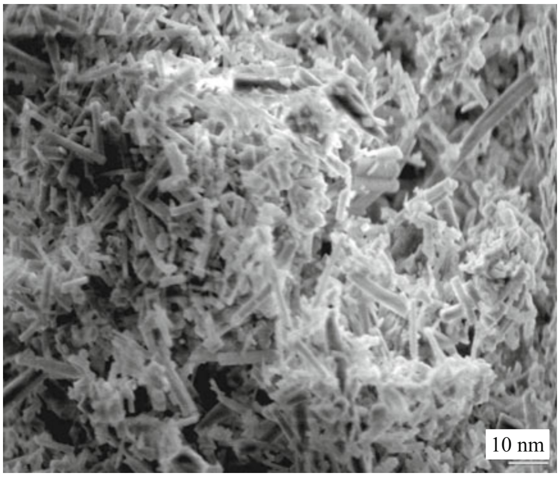

Fig. 7. Structure of VMK-5 material.

In summary, VIAM has developed heat-shielding and heat-insulating materials based on Al_2O_3 fibers for prospective rocket-space engineering and is conducting scientific work on the development of materials with improved thermophysical, radio engineering and physical-mechanical properties, including for complex multifunctional heat-shielding.

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